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Electroluminescence of BaO and SrO phosphors activated by manganese

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A.C. electroluminescence (EL) in BaO . Mn and SrO : Mn powder phosphors is investigated. It is observed that the mean EL brightness is an increasing function of the applied sinusoidal voltage and varies exponentially with the latter It seems that during EL of these phosphors, a Mott-Schottky type of barrier provides the field enhancement The frequency dependence of EL brightness is found to be nonlinear in nature. The brightness waves of the powder cell consist of two major peaks per cycle of the applied voltage It has been inferred that in the present system of phosphors, electroluminescence takes place by impact ionization mechanism

1. INTRODUCTION

It is difficult to excite electroluminescence in such crystalline phosphors, where the percentage of ionic character of bond is very high The reasons for this may be that, (i) there is a short mean free path for electrons and holes, due to their scattering by phonons, (ii) there is a relatively wide forbidden gap between valence and conduction bands and (iii) there is a low concentration of free charge carriers so that the regions where the field is concentrated are not formed (Georgobiani 1964). Alkaline earth oxide phosphors come under the above mentioned group having ionic character of their bonds approx. 70–80%. In order to produce EL from such compounds, it becomes necessary to prepare thin and uniform layers, because, with a reduction in the layer thickness, the development of cascade breakdown becomes more difficult and hence the proportion of electrical energy which goes into ionization of radiation centres is increased while the proportion which goes to heat the crystalline lattice is decreased. The present investigation deals with the studies of EL in BaO : Mn and SrO : Mn by preparing thin and uniform layers of the powder phosphors.

2. EXPERIMENTAL DETAILS

2.1. *Preparation of Phosphors*

BaO : Mn and SrO : Mn electroluminophors were prepared by solid phase reaction through firing the mixture of the starting materials (pure $BaCO_3$ or $SrCO_3 + CaF_2 - 2\% +$ activator compound) in air at 1200°C. The samples were

fired for 4 hours and then slowly cooled to room temperature in about 16 hrs In general, much higher concentration of the activator atoms is required to produce more brightness as reported by many investigators (Zalm 1956, Matossi & Nudelman 1959). The results presented in this paper are those obtained with 5% concentration of Mn/Ba or Mn/Sr. Uniform thin layers of phosphors were deposited on mica sheets using a transparent adhesive substance araldite The use of mica sheet excludes the possibility of carrier injection (Siddalli 1959) at the electrode contacts.

2 2 *Experimental Set-up*

In the present study a non-symmetrical EL cell was used A phosphor layer deposited on thin mica sheet was sandwitched between the electrodes and then it was excited by applying a sinusoidal voltage. A L.F oscillator in conjunction with a wide band amplifier was used for this purpose The output of the amplifier was fed to the two electrodes of the EL cell The mean EL brightness was measured using IP 21 photomultiplier detector coupled with a Rubicon galvanometer (sensitivity 0·0013 μA/mm) The voltage dependence of brightness, keeping other parameters constant, was studied at different frequencies (30 cps to 1000 cps) at room temperature (23°C) Similarly frequency dependence at different fixed voltages was also studied.

For studying the brightness waves, a double beam Tektronix Oscilloscope (type 546) was used in place of the galvanometer The voltage developed across the resistance of the anode circuit of the photomultiplier was amplified and applied to one pair of the Y-plates of the CRO and the exciting voltage was put to the other pair of Y-plates Brightness waves along with the waves of the exciting voltage were photographed for analysis.

3. Results

The powder phosphors prepared with Mn as activator were found to be gray in colour. The darkness in colour increases with increase in Mn-content. This indicates the presence of some other phase in addition to BaO/SrO containing the activator in solid solutions Similar results have been reported by Fisher (1962, 1963) in ZnS : Cu phosphors. Gour & Ranade (1970) and Masoorkar & Ranade (1973) have also confirmed those results in the case of alkaline earth sulphide electroluminophors

3.1. *Voltage and frequency dependence of mean EL brightness*

(a) *BaO : Mn.* The curves representing the mean EL brightness as a function of voltage at fixed frequencies are shown in figure. 1 It is clear from these curves that the increase in brightness is sharper at high voltages than at low voltages The shape of the curves shows that the linear relationship does not

hold well between the brightness (B) and applied voltage (V). Therefore an exponential or power law relation may exist between B and V.

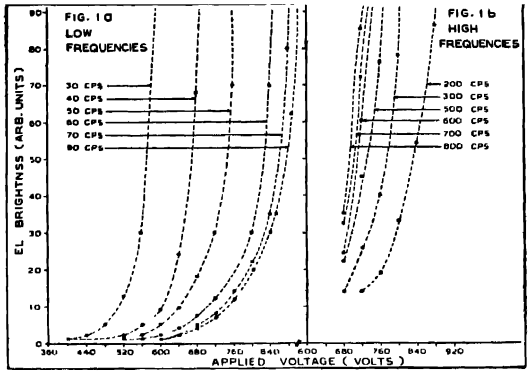

Fig. 1. Voltage dependence of EL brightness of BaO : Mn
(a) at low frequencies,
(b) at high frequencies.

In general, the plots of logarithm of B as an inverse function of $V^{\frac{1}{2}}$ (figure 2) are straight lines. Thus, it can be concluded that the exponential law holds well.

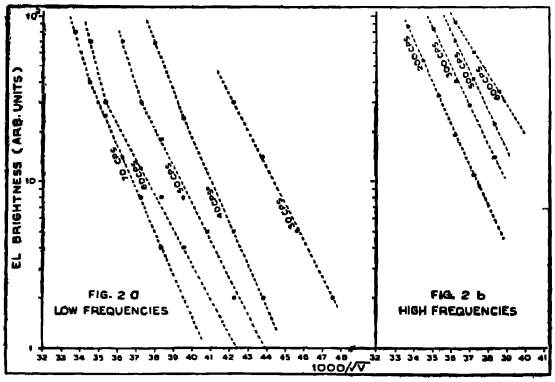

Fig. 2. Voltage dependence of EL brightness (log B Vs $V^{-\frac{1}{2}}$ plots) of BaO : Mn
(a) at low frequencies,
(b) at high frequencies.

The representative curves illustrating the frequency (ν) dependence of brightness ($\log B$ as a function of $\log \nu$) are given in figure 3 The curves are observed to be non-linear in nature, that is, at fixed voltages, brightness first decreases with frequency (from 30 cps to 100 cps) and then it starts increasing more rapidly than linearly, with increase in frequency. No saturation occurs

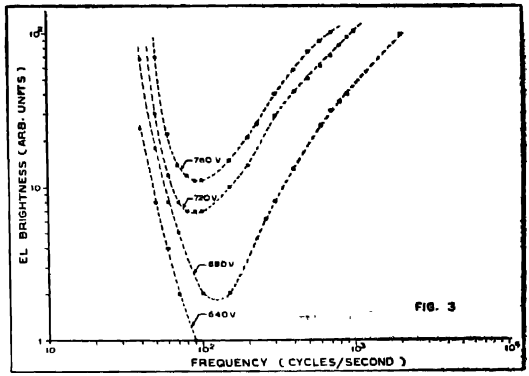

Fig. 3. Frequency dependence of EL brightness at fixed voltages of BaO : Mn

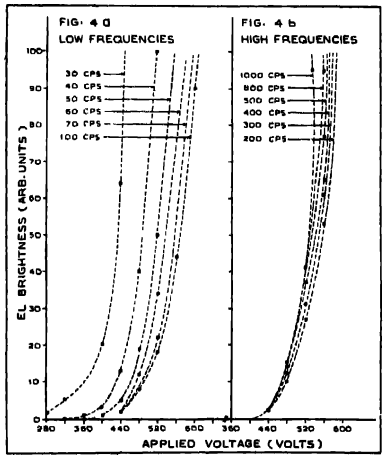

Fig. 4. Voltage dependence of EL brightness of SrO : Mn
(a) at low frequencies,
(b) at high frequencies,

upto about 1000 cps. It is quite possible that the saturation might occur at higher frequencies (> 1000 cps), which was not tried in the present study.

(b)*SrO : Mn.* The voltage dependence of B at various frequencies in SrO : Mn phosphors is shown in figure 4. Since $\log B$ Vs. $V^{-\frac{1}{2}}$ curves are all linear (figure 5), it can be concluded that the exponential law holds here too.

The Fig. 6 depicts the relationship between frequency and brightness at constant voltages. Here also the curves are all non-linear and therefore no empirical relationship between B and ν was found to hold well. In SrO : Mn phosphors the saturation in brightness is observed after ~600 cps. at higher voltages

3 2. *Brightness Waves*

In all the cases, two emission peaks within one cycle of the applied sinusoidal voltage are observed (Figs 7 & 8) At fixed frequencies, the amplitude of both peaks increases with an increase of voltage for BaO : Mn (Figs. 7a & b) and SrO · Mn (Figs, 8a & b) phosphors

4 Discussion

4 1. *Voltage Dependence*

It is found practically in both types of phosphors (BaO · Mn and SrO : Mn) that the mean EL brightness is an increasing function of the voltages Qualitatively, all the phosphors have similar type of dependence. It can be understood on this basis that initially the number of particles in which the electroluminescence takes place is small, but on increasing the voltage, more and more active regions are exposed to voltage gradients above the threshold level The plots between $\log B$ and $V^{\frac{1}{2}}$ presented in the figures 2 and 5 show almost linear relationship for different frequencies. Thus the following relationship between the mean EL brightness (B) and voltage (V) seems to hold well.

$$B = B_0 \exp(-C/V^{\frac{1}{2}}) \qquad \ldots \quad (1)$$

(B_0 and C being the constants).

Very close agreement of the experimental curves (figures 2 and 5) with the theoretical formula (1) indicates the existence of a Mott-Schottky barrier in the present system of phosphors The square root term in the exponential dependence of brightness and voltage can be interpreted on the basis of the acceleration —collision mechanism by taking the probability of impact—ionization to be proportional to $\exp(-C'/E)$, E being the electric field and C' a constant along with the fact that E itself is proportional to $V^{\frac{1}{2}}$ in Mott-Schottkey barrier.

4.2. *Frequency Dependence*

In the most general sense, a certain amount of light is expected to be generated at each instant, the luminous condenser is charged or discharged. It is assumed that the EL brightness can be regarded as being due to instantaneous concentra-

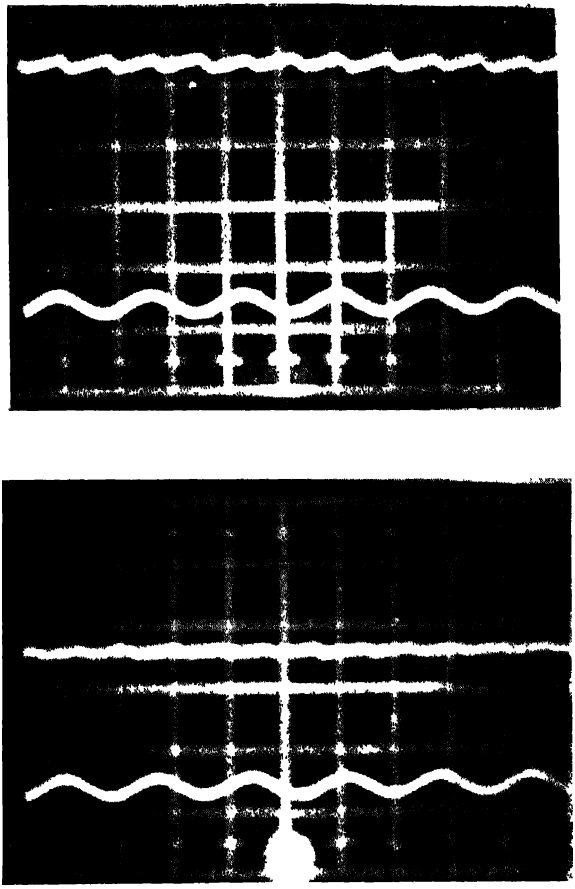

Fig. 7. Oscillograms of BaO : Mn at 30 cps (sweep duration 2 m-sec/cm). (a) at 680 volts; (b) at 720 volts. The curve (1) is the wave form of the applied voltage while the curve (2) is the cwave form of the light emitted from the EL cell.

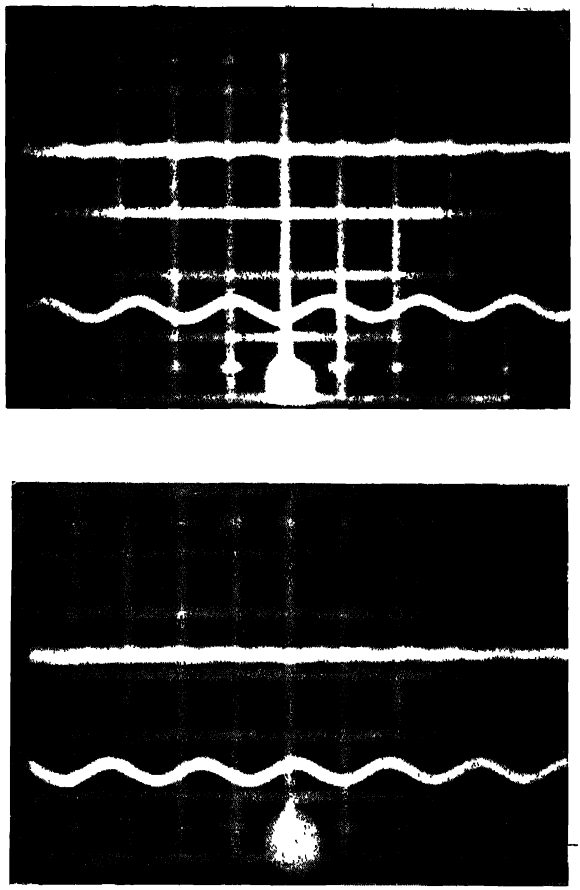

Fig. 8. Oscillograms of SrO : Mn at 30 cps (sweep duration 20 m-sec/cm). (a) at 520 volts; (b) at 560 volts. The curve (1) is the wave form of the applied voltage and the curve (2) is the wave form of the light emitted from the EL cell.

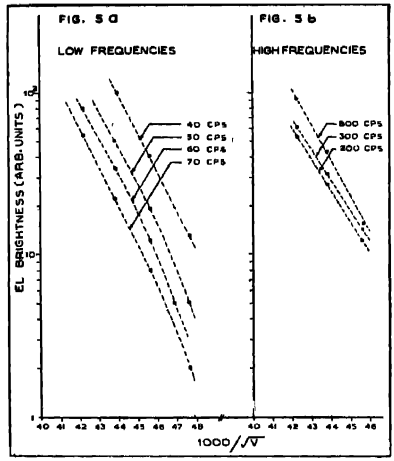

Fig. 5. Voltage dependence of EL brightness (log B Vs $V^{-\frac{1}{2}}$ plots) of SrO : Mn
(a) at low frequencies,
(b) at high frequencies.

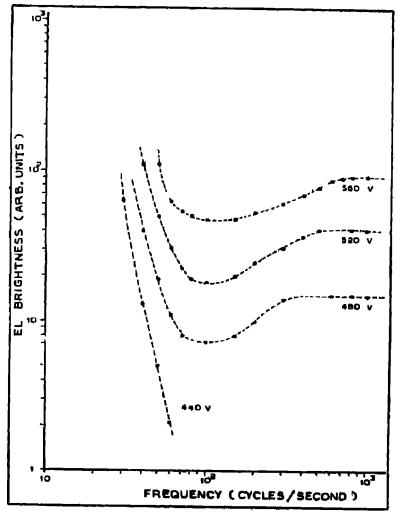

Fig. 6. Frequency dependence of EL brightness at fixed voltages of SrO : Mn.

tion of light emitting point sources. At high frequencies, the emitting point-sources will be larger and hence greater would be the emitted light The experimental observation that the EL brightness increases with frequency from 100 cps onwards (figures 3 and 6) confirms this view. However, the peculiar behaviour of decrease in B with increase in frequency within the range 30 to 100 cps in both types of phosphors is observed. This may be attributed to be due to the polariza tion effects.

The increase in EL brightness above 100 cps can be understood on the basis that emptying and refilling of the luminescent centres takes place more rapidly with increase in frequency (Ivey 1957). When the time period of the applied AC cycle becomes comparable with the life time of excited electron, the increasing frequencies can not impart a proportional increase in average intensity as the electron does not have enough time to emerge out from the trap. Hence saturation can be expected in the higher frequency range which was experimentally observed in the case of SrO : Mn (figure 6)

4 3. *Brightness Waves*

Bitter & Waymouth (1954) have shown that the light emission from a single grain is concentrated in certain small spots These spots emit brightness waves. According to Thornton (1956), it can be assumed that these spots behave as minia ture rectifying junctions Some of the junctions will be excited on the application of one half cycle while others on the application of the other half cycle. In this way, two peaks are expected in one complete cycle of applied field, which was experimentally observed in the present system of phosphors (Figs 7 and 8).

Acknowledgments

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